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(71) Applicant: FINA RESEARCH S.A.
B-7181 Seneffe (Feluy) (BE)

(72) Inventors:
- Razavi, Abbas
7000 Mons (BE)
- Bellia, Vincenzo
7110 Maurage (BE)

(54) **Metallocene catalyst component for use in producing isotactic polyolefins**

(57) A metallocene catalyst component for use in preparing isotactic polyolefins, which component has the general formula:

$$R''(C_pR_1R_2)(C_p'R_n')\,MQ_2 \qquad (I)$$

wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R" is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^*_3 in which X is chosen from Group IVA, and each R* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned *non-vicinal* to the distal substituent and is of the formula $YR\#_3$ in which Y is chosen from group IVA, and each R# is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \le n \le 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

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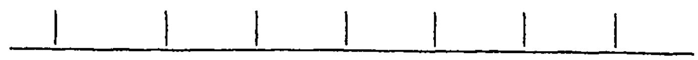
Description

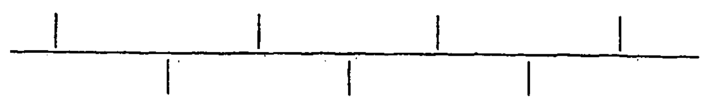
The present invention relates to a metallocene catalyst component for use in preparing isotactic polyolefins, especially polypropylenes. The invention further relates to a catalyst system which incorporates the metallocene catalyst component and a process for preparing such isotactic polyolefins.

Olefins having 3 or more carbon atoms can be polymerised to produce a polymer with an isotactic stereochemical configuration. For example, in the polymerisation of propylene to form polypropylene, the isotactic structure is typically described as having methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer. This can be described using the Fischer projection formula as follows:



Another way of describing the structure is through the use of NMR spectroscopy. Bovey's NMR nomenclature for an isotactic pentad is ... mmmm with each "m" representing a "meso" diad or successive methyl groups on the same side in the plane.

In contrast to the isotactic structure, syndiotactic polymers are those in which the methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. Using the Fischer projection formula, the structure of a syndiotactic polymer is described as follows:



In NMR nomenclature, a syndiotactic pentad is described as ...rrrr... in which "r" represents a "racemic" diad with successive methyl groups on alternate sides of the plane.

In contrast to isotactic and syndiotactic polymers, an atactic polymer exhibits no regular order of repeating unit. Unlike syndiotactic or isotactic polymers, an atactic polymer is not crystalline and forms essentially a waxy product.

While it is possible for a catalyst to produce all three types of polymer, it is desirable for a catalyst to produce predominantly an isotactic or syndiotactic polymer with very little atactic polymer. C_2-symmetric metallocene catalysts are known in the production of the polyolefins. For example, C2 symmetric *bis* indenyl type zirconocenes which can produce high molecular weight high melting isotactic polypropylene. The preparation of this metallocene catalyst is costly and time-consuming, however. Most importantly, the final catalyst consists of a mixture of racemic and meso isomers in an often unfavourable ratio. The meso stereoisomer has to be separated to avoid the formation of atactic polypropylene during the polymerisation reaction.

EP-A-0537130 discloses the use of a C1 symmetric metallocene catalysts for the production of isotactic polypropylene. A preferred catalyst is isopropylidine (3-tert butyl-cyclopentadienyl-fluorenyl) $ZrCl_2$. This catalyst has a bulky t-butyl group positioned on the cyclopentadienyl ring distal to the isopropylidine bridge. This catalyst has the advantage that it consists of only one stereoisomer and so no isomeric metallocene separation is required at the final stage of its synthesis. Whilst polypropylene preparation using this catalyst produces isotactic polypropylene, the polymer product has poor mechanical properties because of the presence of regiodefects and relatively low molecular weight.

Regiodefects occur in the polymer chain when, instead of producing a perfect isotactic polyolefin in which each monomeric unit is positioned head-to-tail in relation to the next, mis-insertions of the monomers occur so as to give either a head-to-head or tail-to-tail mis-match. In the polymerisation process according to EP-A-0619325, there is a typical mis-insertion frequency of around 0.4%. These so called (2-1) regiodefects are partially transferred to the so called (1-3) insertion through an isomerisation process leaving units of four CH_2 groups in the backbone of the polypropylene chain. This has a deleterious effect on the physical and mechanical properties of the polymer and results in low molecular weight isotactic polypropylene with a low melting point.

The present invention aims to overcome the disadvantages of the prior art.

In a first aspect, the present invention provides a metallocene catalyst component for use in preparing isotactic

polyolefins, which component has the general formula:

$$R''(C_pR_1R_2)(C_p'R_n')\,MQ_2 \qquad (I)$$

wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R" is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^*_3 in which X is chosen from Group IVA, and each R* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned *non-vicinal* to the distal substituent and is of the formula $YR\#_3$ in which Y is chosen from group IVA, and each R# is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

Polyolefins produced using the metallocene catalyst component of the present invention are not only found to be isotactic but are also found to be substantially free of regiodefects. Accordingly, the polyolefins produced thereby have improved mechanical properties including a high weight average molecular weight typically of the order of 150,000-600,000 and elevated melting point. Without wishing to be bound by any theory, it is postulated that the bulky group on the cyclopentadienyl ring contributes to the stereospecificity of the polymerisation reaction whereas the proximal substituent on the cyclopentadienyl ring contributes to the regiospecificity of monomer insertion and the increase of molecular weight.

In the bulky distal substituent group R_1, X is preferably C or Si. R* may be a hydrocarbyl such as alkyl, aryl, alkenyl, alkylaryl or aryl alkyl, preferably methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. R_1 may comprise a hydrocarbyl which is attached to a single carbon atom in the cyclopentadienyl ring or may be bonded to two carbon atoms in that ring. Preferably, R_1 is $C(CH_3)_3$, $C(CH_3)_2Ph$, CPh_3 or $Si(CH_3)_3$, most preferably $C(CH_3)_3$.

The proximal substituent R_2 is preferably CH_3.

The structural bridge R" is preferably alkylidene having 1 to 20 aliphatic or aromatic carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphene or amine bridging the two C_p rings. R" is preferably isopropylidene in which the two C_p rings are bridged at position 2 of the isopropylidene.

M is preferably zirconium or titanium, most preferably zironium. Q may be a hydrocarbyl such as alkyl, aryl, alkenyl, alkylaryl or aryl alkyl, preferably methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. Q is preferably a halogen.

The fluorenyl ring C_p' can have up to 8 substitutuent groups R'_n, each of which is the same or different and may be a hydrocarbyl selected from alkyl, aryl, alkenyl, alkyl aryl or aryl alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. These substituents must be selected so that they do not interfere with coordination of the monomer to the metal. Preferably, therefore, the fluroenyl ring is unsubstituted at both positions 4 and 5, these positions being distal to the bridge.

In a further aspect, the present invention provides a metallocene catalyst component for use in preparing isotactic polyolefins, which comprises *(i)* a catalyst component as defined above; and *(ii)* a regioisomer thereof in which R_2 is proximal to the bridge and positioned *vicinal* to the distal substituent.

Such regioisomers are frequently relatively easy to prepare because they are formed as a "by-product" during the synthetic route by which the catalyst component (i) may be made.

Surprisingly, it has been found that catalyst components including both regioisomers can be used in the preparation of isotactic polyolefins which have a multimodal, especially a bimodal, molecular weight distribution.

In a further aspect, the present invention provides a catalyst system for use in preparing isotactic polyolefins, which comprises (a) a catalyst component as defined above; and (b) an aluminium- or boron-containing cocatalyst capable of activating the catalyst component. Suitable aluminium-containing cocatalysts comprise an alumoxane, an alkyl aluminium and/or a Lewis acid.

The alumoxanes usable in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula:

$$(\mathrm{I})\quad R\text{-}(\underset{\displaystyle R}{\underset{|}{Al}}\text{-}O)_n\text{-}AlR_2$$

for oligomeric, linear alumoxanes and

$$(\mathrm{II})\quad (\text{-}\underset{\displaystyle R}{\underset{|}{Al}}\text{-}O\text{-})_m$$

for oligomeric, cyclic alumoxane,
wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

Suitable boron-containing cocatalysts may comprise a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula $[L'\text{-}H] + [B\ Ar_1\ Ar_2\ X_3\ X_4]^-$ as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

The catalyst system may be employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons with 4 to 7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finally divided form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene.

Preferably, the support is a silica having a surface area comprised between 200 and 700 m^2/g and a pore volume comprised between 0.5 and 3 ml/g.

The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is in the range between 1:1 and 100:1, preferably in the range 5:1 and 50:1.

The order of addition of the metallocenes and alumoxane to the support material can vary. In accordance with a preferred embodiment of the present invention alumoxane dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the metallocene catalyst component is added to the slurry.

Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperature and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.

Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material.

In a further aspect, the present invention provides use of a catalyst component as defined above and a cocatalyst which activates the catalyst component, for the preparation of isotactic polyolefins, preferably polypropylenes. In a still further aspect, the present invention provides use of a metallocene catalyst component comprising *(i)* the catalyic component and *(ii)* a regioisomer thereof, in which R_2 is proximal to the bridge and positioned *vicinal* to the distal substituent, for the preparation of isotactic polyolefins, especially polypropylenes, having a multimodal molecular weight distribution, preferably a bimodal molecular weight distribution.

In a further aspect, the present invention provides a process for preparing isotactic polyolefins, especially polypropylenes, which comprises contacting a catalyst system as defined above with at least one olefin, preferably propylene,

in a reaction zone under polymerisation conditions.

The catalyst component may be prepared by any suitable method known in the art. Generally, the preparation of the catalyst component comprises forming and isolating bridged dicyclopentadiene, which is then reacted with a halogenated metal to form the bridged metallocene catalyst.

In one embodiment, the process for preparing the bridged metallocene catalyst components comprises contacting a substituted cyclopentadiene having bulky and non bulky substituents on the cyclopentadienyl ring with a fluorene under reaction conditions sufficient to produce a bridged substituted dicyclopentadiene. The process further comprises contacting the bridged substituted dicyclopentadiene with a metal compound of the formula MQ_k as defined above under reaction conditions sufficient to complex the bridged dicyclopentadiene to produce a bridged metallocene wherein M and Q are each defined as above and $0 \leq k \leq 4$. The process step of contacting the bridged substituted dicyclopentadiene with a metal compound can be performed in a chlorinated solvent.

In a further embodiment, the process comprises contacting a substituted cyclopentadiene having bulky and non bulky substituents on the cyclopentadienyl ring with an alkyl silyl chloride of the formula $R\sim_2$ Si Hal_2 wherein R~ is a hydrocarbyl having 1 to 20 carbon atoms and Hal is a halogen. A second equivalent of an optionally substituted fluorene is added to produce a silicon bridged disubstituted cyclopentadienyl-fluorenyl ligand. The subsequent steps are similar to those above for producing a bridged disubstituted cyclopentadienyl-fluroenyl ligand coordinated to metals such as Zr, Hf and Ti.

In a further embodiment, the process comprises contacting a substituted cyclopentadiene with a fulvene producing agent such as acetone to produce a substituted fulvene. Subsequently, in a second step, the fulvene is reacted with fluorene to produce a carbon bridged substituted cyclopentadienyl-fluorenyl ligand that will produce the desired metallocene catalysts after reacting with MCl_4, in which M is Zr, Hf or Ti.

The invention will now be described in further detail, by way of example only, with reference to the attached drawings in which:

FIGURE 1 shows an illustration of the three-dimensional structure of a preferred catalyst component of the present invention as obtained by X-ray diffraction analysis of isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2;

FIGURE 2 shows an illustration of the three-dimensional structure of a preferred catalyst component of the present invention as obtained by X-ray diffraction analysis of isopropylidene (3-tert. butyl-2-methyl cyclopentadienyl-fluorenyl) Zr Cl_2;

FIGURE 3 shows the results of gel permeation chromotography on isotactic polypropylene produced at 40°C using a mixture of the isomers shown in Figures 1 and 2 as a catalyst component; and

FIGURE 4 shows the results of gel permeation chromotography on isotactic polypropylene produced at 60°C using a mixture of the isomers shown in Figures 1 and 2 as a catalyst component.

Example 1: Synthesis of isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2.

A) Synthesis of the trimethyl fulvene.

In a round bottom flask equipped with magnetic stirring bar and nitrogen inlet is placed 350 ml of methanol (at -78°C) containing freshly prepared methylcyclopentadiene under nitrogen. To this solution is added a solution of 28.6 g of acetone in 50 ml of methanol drop wise. Subsequently 52.5 g of pyrolidene is added. The reaction mixture is stirred at ambient temperature for 24 hours. After neutralization with acetic acid and separation of the organic phase the solvent is evaporated and the remaining yellow oil is subjected to distillation. A mixture of 6,6,3-trimethyl fulvene and 6,6,5,-trimethyl fulvene is obtained in 65% yield.

B) Synthesis of methyl-tert.butyl-cyclopentadiene.

The product obtained in step A is placed in 21 flask and dissolved in 350 ml of diethyl ether and cooled down to 0°C. To the solution is added drop wise 140.6 ml of methyl lithium in ether (1.6 mol). The reaction is completed after a few hours. After adding 40 ml of saturated solution of NH_4Cl in water the organic phase is separated and dried with $MgSO_4$. The evaporation of the solvent leads to the isolation of a yellow oil as two stereo isomers quantitatively.

C) Synthesis of tertbutyl-trimethyl-fulvene.

In a 500 ml flask is placed 12.60 g of the product obtained in step B and dissolved in 40 ml of methanol. The mixture is cooled down to -78°C. 2.15 g acetone in 10 ml of ethanol is added slowly. In the next step 4 g of pyrolidene in 10 ml of methanol is added. After six hours the reaction is terminated by addition of 10 ml of acetic acid. After separation of organic phase, drying, evaporation of solvents and distillation an orange oil is obtained (8.95 g).

D) Synthesis of 2,2- [(3-tertbutyl-methyl-cyclopentadienyl)-fluorenyl]-propane.

In round bottom flask is placed 3.8 g fluorene in 100 ml of THF under nitrogen. 14.2 ml of methyl lithium in ether (1.6 mol) is added. The reaction mixture is stirred for 3 hours and then reacted with 4.70 g of the product obtained in step C dissolved in 10 ml of THF. The reaction is terminated after 8 hours by the addition of a saturated solution of NH_4Cl in water. The organic phase is separated, the solvents evaporated and 8.5 g of the title compound is obtained as an oily mixture of two principal isomonomers, 2,2-[(3-tertbutyl-5-methyl-cyclopentadienyl)-fluorenyl]-propane and 2,2-[(3-tertbutyl-2-methyl-cyclopentadienyl)-fluorenyl]-propane.

E) Synthesis of the mixture of isopropylidene(3-tertbut-5-methyl-cyclopentadienyl)-fluorenyl)$ZrCl_2$ (1) and isopropylidene (3 -tertbut-2-methyl-cyclopentadienyl)-fluorenyl)$ZrCl_2$ (2).

2 g of the ligand obtained in step D is dissolved in 250 ml THF under nitrogen and reacted with 7.3 ml methyl lithium in ether (1.6 mol). The reaction mixture is stirred over night. The solvent is evaporated next day and the dianion of the ligand is isolated which is reacted with 3.8 g of ZrC14 in 200 ml ether at -78°C. The mixture is stirred for 6 hours at room temperature. The two isomers can be separated by solvent separation since (1) is less soluble in dichloromethane than (2).

Isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2 is recovered, the structure of which is shown in Figure 1.

Example 2: Synthesis of isopropylidene (3-tert. butyl-2-methyl-cyclopentadienyl-fluorenyl) Zr Cl2.

The synthetic procedure according to Example 1 is followed except that, after solvent separation at the end of step E, isopropylidene (3-tert. butyl-2-methyl cyclopentadienyl-fluorenyl) Zr Cl_2 is recovered. The structure of this isomer is shown in Figure 2.

sp

Example 3: Synthesis of mixture of isopropylidene (3-tert.butyl-5-methyl(cyclopantadienyl-fluorenyl) Zr Cl_2 and isopropylidene (3-tert. butyl-2-methyl cyclopantadienyl-fluorenyl) Zr Cl_2.

sp

The synthetic procedure according to Example 1 is followed except that the step of solvent separation of the two isomers is omitted.

Example 4: Polymerisation procedures

Each polymerisation was performed in a 4 litre bench reactor with pure polypropylene or with diluent such as cyclohexane or isobutane with the quantities reported in the following Tables. Polymerisation was initiated by introducing metallocene (0.5 to 5 mg) precontacted with 1 ml of MAO (methylaluminoxane) (30% solution in toluene obtained from WITCO) three minutes prior to its introduction into the reactor.

Tables 1 and 2 show the results of polypropylene production using the catalyst system of Example 1. Entries 1 to 4 compare polymerisation of pure polypropylene (bulk - entry 1) with those using the diluents cyclohexane (entry 2) and isobutane at two different partial pressures of hydrogen (entries 3 and 4). The polymerisation temperature for each of these entries was 60°C. Entries 5 and 6 compare bulk propylene polymerisation at the higher temperatures of 70°C and 80°C respectively. It is apparent that a molecular weight of about 200,000 to about 450,000 was obtainable. Polypropylene having a melt temperature of at least 139°C was obtained, in this case around 140°C. The polymers obtained exhibited monomodality on gel permeation chromatography (results not shown).

Table 1

Polymerization with iPr(5-Me-3tBu-Cp)FluZrC1$_2$									
Entry	Pol. Temp (°C)	Hourly prod. (gPP/gCat/h)	MI$_2$ (g/10min)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	60	54,000	3.64	67,700	458,500	1,334,000	6.8	2.9	142.4
2	60	50,500	1.74	120,000	402,200	936,000	3.4	2.3	143.8
3	60*	96,000	3.08	74,400	333,800	880,000	4.5	2.6	142.6
4	60**	110,000	13.56	68,000	248,600	581,000	3.7	2.3	142.2
5	70	110,500	7.53	74,200	306,000	1,066,000	4.1	3.5	139.3
6	80	130,000	13.50	62,800	213,900	499,000	3.4	2.3	139.6
Key: MI$_2$ = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight; D = Mw/Mn; D' = Mz/Mw 1. Bulk Propylene; 2. Slurry in Cyclohexane; 3. Slurry in isobutane									

(*): 0.25 Nl H2;
(**): 1 Nl H2

No Tcry

Table 2 shows the microtacticity of the polymer obtained using the catalyst according to Example 1 under polymerisation conditions as defined by the corresponding entries in Table 1. The results were obtained using ^{13}C NMR spectroscopy. It will be apparent that the polypropylene contained more than 80% of pentads in the purely isotactic form (mmmm) and a virtually undetectable frequency of misinsertions.

Tables 3 and 4 show corresponding data in relation to the bulk polymerisation of propylene using the catalyst system of Example 2. The weight average molecular weight of the polypropylene in this case is much lower than for the polypropylene produced using the catalyst of Example 1. The melt temperatures reported in Table 3 are also lower than those in Table 1. Table 4 shows the microtacticity of the polymers of the two entries in Table 1 from which it will be apparent that the percentage of purely isotactic pentads is reduced as compared with those reported in Table 2. Importantly, a misinsertion frequency of up to 0.4% is found in Table 4 as compared with the virtually undetectable frequency of misinsertions reported in Table 2.

Table 2

Microtacticity with iPr(5-Me-3tBuCp)FluZrC1$_2$						
Entry	mmmm%	mmmr%	mmrr%	mrrm%	inversion %	NMR Scans
1	85.8	5.3	5.1	2.5	not det.	2224
2	86.8	5.2	4.7	2.3	(1)	4080
3	83.9	6.1	5.3	2.5	(1)	4344
4	84.0	5.8	5.2	2.5	(1)	2368
5	82.8	6.3	5.6	2.7	/	2272
6	83.8	6.2	5.4	2.4	(1)	7128
(1): inversions observed but too low to be quantified.						

Table 3

Bulk polymerization with iPr(2-Me-3tBuCp-FluZrC1$_2$								
Entry	Pol. Temp (°C)	Hourly prod. (gPP/gCat/h)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	40	179,000	37,400	96,600	409,000	2.6	4.2	101.4
2	60	99,000	22,100	73,800	431,000	3.3	5.8	110.9
Key: MI$_2$ = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight; D = Mw/Mn; D' = Mz/Mw								

Table 4

Microtacticity with iPr(2-Me-3tBuCp)FluZrC1$_2$							
Entry	Pol.Temp. (°C)	mmmm%	mmmr%	mmrr%	mrrm%	Inv. %	NMR Scans
1	40	61.1	12.3	13.4	6.0	0.2-0.4	5000
2	60	69.3	10.6	10.3	4.9	0.1-0.2	3976

Table 5

Bulk polymerization with the mixture of isomers iPr(2-Me-3tBuCp)FluZrC1$_2$ + iPr(5-Me-3tBuCp)FluZrC1$_2$								
Entry	Pol. Temp (°C)	Hourly prod. (gPP/gCat/h)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	40	2,250	27,800	336,700	1,524,000	12.1	4.5	133.1
2	60	5,200	45,700	255,000	906,800	5.6	3.6	136.7
Key: MI$_2$ = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight; D = Mw/Mn; D' = Mz/Mw								

Tables 5 and 6 show the results of corresponding bulk propylene polymerisation with a mixture of the two isomers from Examples 1 and 2. These polymers have relatively high melt temperatures. However, unlike the polymers reported in Table 1 using the single isomer isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl$_2$ which exhibits monomodality on gel permeation chromatography, polymers produced using the mixture of isomers exhibit bimodality. This is apparent from Figures 3 and 4 which show respectively the results of gel permeation chromatography on the polymers of entries 1 and 2 of Table 5.

Table 6 shows steric pentad concentrations and regiodefects concentrations.

Table 6

iPr(2-Me-3tBuCp)FluZrC1$_2$ + iPr(5-Me-3tBuCp)FluZrC1$_2$						
Entry	Pol.Temp (°C)	mmmm%	mmmr%	mmrr%	mrrm%	Inv. %
1	40	62.0	10.6	11.8	4.8	0.3
2	60	74.3	8.2	8.17	3.65	nd

Claims

1. A metallocene catalyst component for use in preparing isotactic polyolefins, which component has the general formula:

$$R''(C_pR_1R_2)(C_p'R_n')\,MQ_2 \qquad (I)$$

wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R" is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^*_3 in which X is chosen from Group IVA, and each R^* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned *non-vicinal* to the distal substituent and is of the formula $YR\#_3$ in which Y is chosen from group IVA, and each R# is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

2. A catalyst component according to claim 1, wherein R_1 is $C(CH_3)_3$, $C(CH_3)_2Ph$, CPh_3 or $Si(CH_3)_3$.

3. A catalyst component according to claim 2, wherein R_1 is $C(CH_3)_3$.

4. A catalyst component according to any one of claims 1 to 3, wherein Y is carbon.

5. A catalyst component according to claim 4, wherein R_2 is CH_3.

6. A catalyst component according to any one of the preceding claims, wherein R" is alkylidene having 1 to 20 carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphine or amine.

7. A catalyst component according to claim 6, wherein R" is isopropylidene.

8. A catalyst component according to any one of the preceding claims, wherein M is zirconium or titanium.

9. A catalyst component according to any one of the preceding claims, wherein Q is halogen.

10. A catalyst component according to any one of the preceding claims, wherein the fluorenyl ring is unsubstituted at both positions 4 and 5.

11. A metallocene catalyst component for use in preparing isotactic polyolefins, which component comprises isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2.

12. A metallocene catalyst component for use in preparing isotactic polyolefins, which comprises *(i)* a catalyst component according to any one of the preceding claims; and *(ii)* a regioisomer thereof in which R_2 is proximal to the bridge and positioned *vicinal* to the distal substituent.

13. A metallocene catalyst component for use in preparing isotactic polyolefins, which comprises isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2 and isopropylidene (3-tert. butyl-2-methyl cyclopentadienyl-fluorenyl) Zr Cl_2.

14. A catalyst system for use in preparing isotactic polyolefins, which comprises (a) a catalyst component according to any one of the preceding claims; and (b) an aluminium- or boron-containing cocatalyst capable of activating the catalyst component.

15. A catalyst system according to claim 14, which further comprises an inert support.

16. Use of a catalyst component according to any one of claims 1 to 11, and a cocatalyst which activates the catalyst component, for the preparation of isotactic polyolefins.

17. Use of a catalyst component according to claim 12 or claim 13, and a cocatalyst which activates the catalyst com-

ponent, for the preparation of isotactic polyolefins having a multimodal molecular weight distribution.

18. A process for preparing isotactic polyolefins, which comprises contacting a catalyst system according to claim 14 or claim 15 with at least one olefin in a reaction zone under polymerisation conditions.

19. A process according to claim 18, wherein the olefin is propylene.

3 tert butyl
5-methyl

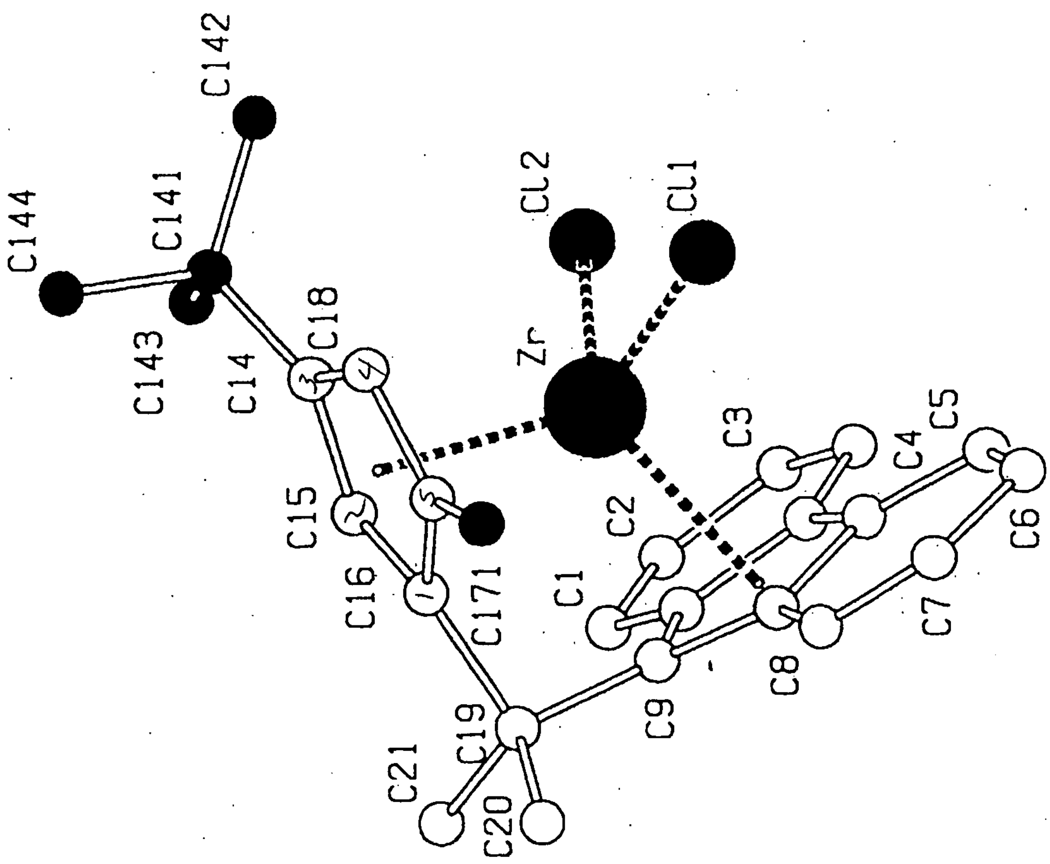
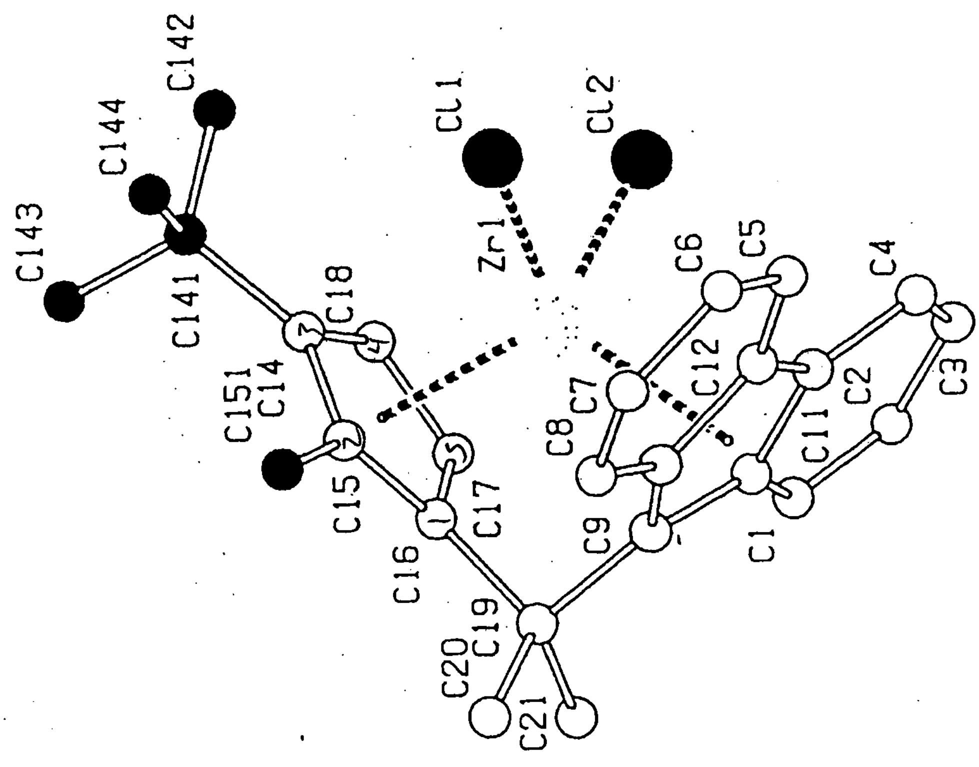


FIGURE 1

3 tert butyl 2 methyl

FIGURE 2



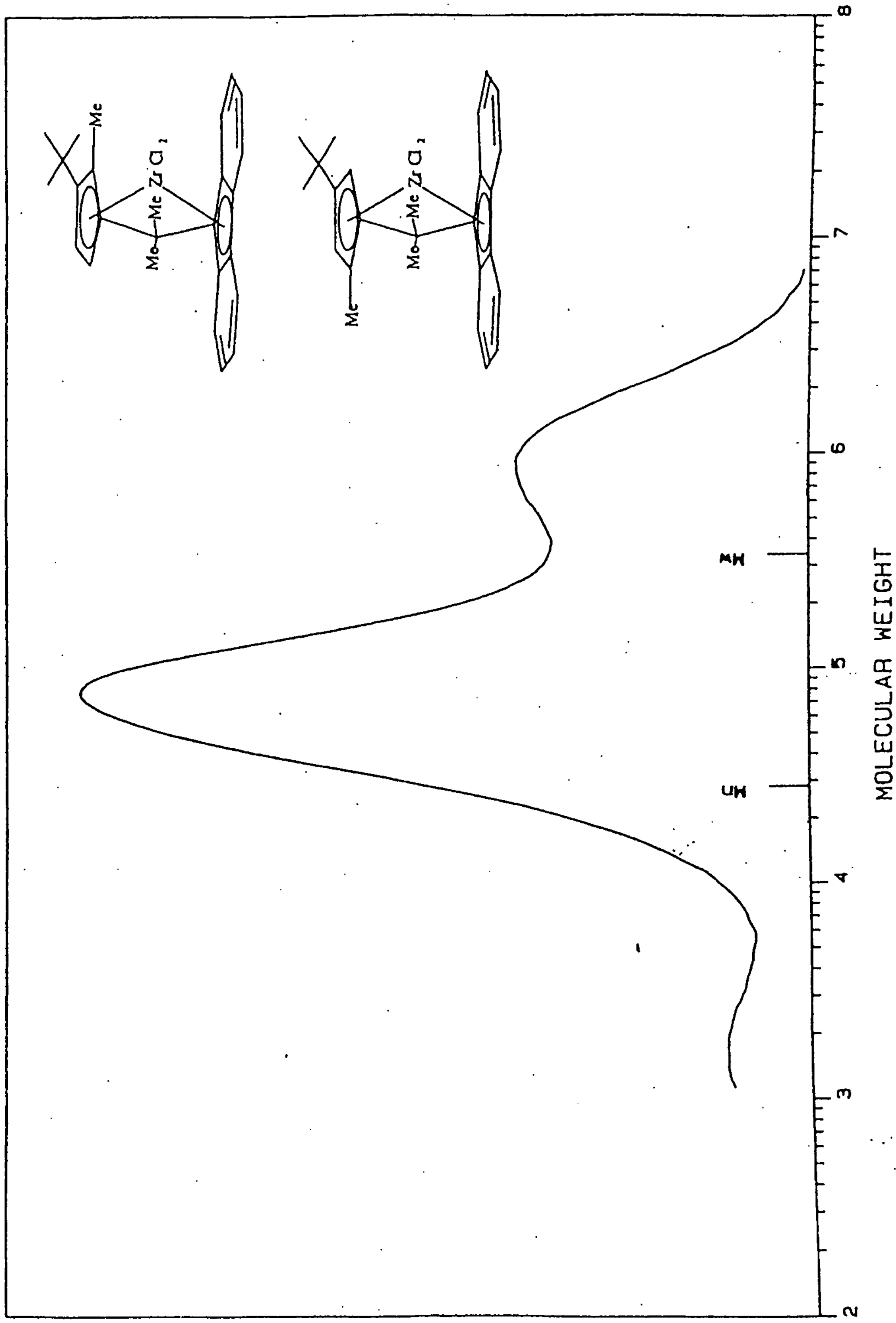

Me
Me
Me
Me
Zr Cl2
Me
Me
Me
Zr Cl2
Mw
Mn
2
3
4
5
6
7
8
MOLECULAR WEIGHT

FIGURE 3

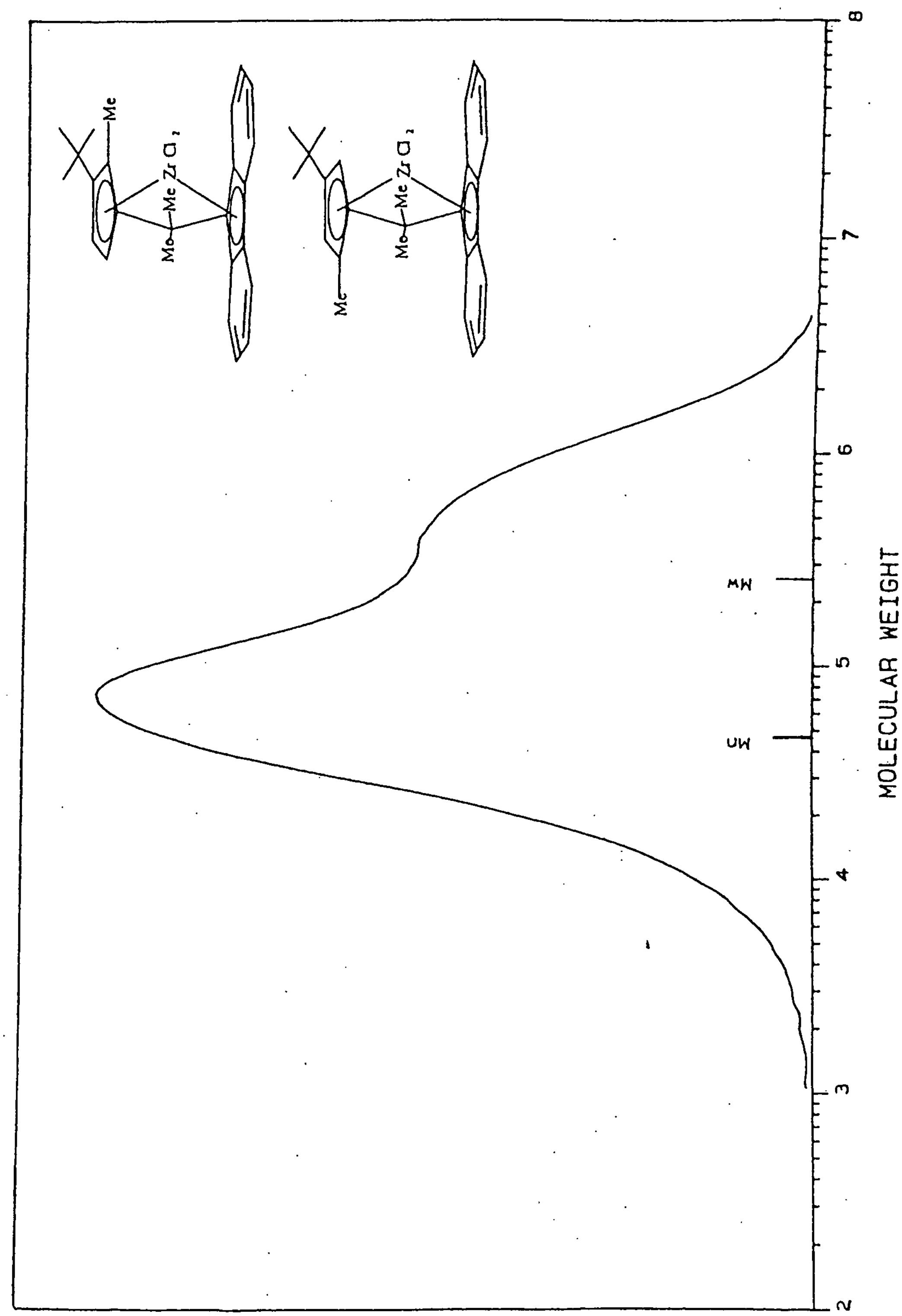


FIGURE 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8467

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 459 117 A (EWEN JOHN A) * claims; col. 8, lines 21-27; col. 4, 29-30 and 42 * ---	1-19	C08F10/00 C08F4/642
D,A	EP 0 537 130 A (FINA TECHNOLOGY) * claims * ---	1-19	
A	EP 0 747 406 A (FINA TECHNOLOGY) * claims * ---	1-19	
A	EP 0 693 497 A (DANUBIA PETROCHEM POLYMERE) * claims * -----	1-19	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C08F
C07F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 August 1997	Mergoni, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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